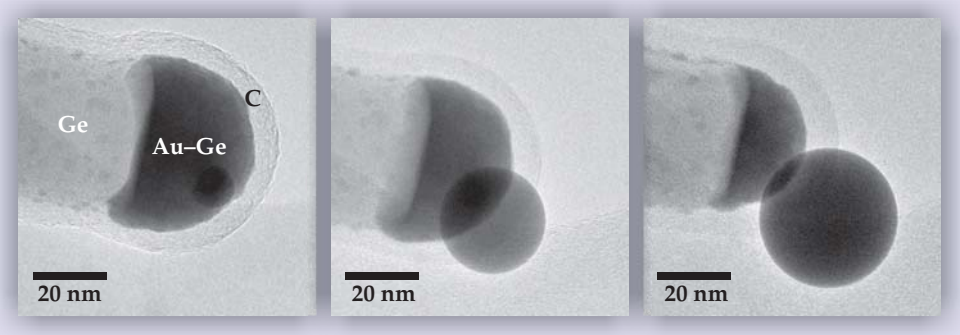
Nanowire pipette dispenses zeptoliter drops of liquid metal

To make a droplet out of just a few thousand atoms and then measure it is tricky. Thermodynamically, a drop that size is exceedingly delicate and can abruptly evaporate or freeze. The drive to reduce its free energy can also prompt a drop on a surface to shrink or grow at its neighbors' expense, a process known as Ostwald ripening. And the huge surface-to-volume ratio makes it prone to contamination from stray impurities.

Two physicists from Brookhaven National Laboratory have now developed an exotic approach to the challenge. Last year, Peter Sutter and Eli Sutter figured out how to coat a germanium nanowire with a protective carbon shell using the beam of a transmission electron microscope (TEM) in high vacuum. During that study, the husband–wife team realized that the process, with just a few modifications, would enable them to transform the coated nanowire into a syringe or pipette of sorts that could hold and extrude, in situ, zeptoliter (10^{-21} L) volumes of liquid metal.[1]



Germanium doesn't react with carbon, but a small amount of gold added to the wire during its growth catalyzes the self-assembly of graphene sheets that encapsulate it. The researchers found that if they heated the wire above its eutectic temperature—the melting point of the combined Au–Ge mixture, typically hundreds of degrees lower than that of either element—they could concentrate a gold-rich melt at the end of the germanium wire. Training the TEM's electron beam onto that region shrinks the curved carbon shell and raises the pressure within the shell to gigapascals. Further narrowing the beam to a tight (roughly 1 nm) focus on the tip of the shell produces a high enough concentration of defects to open it, and elastic relaxation forces the fluid outward.

The large pressure gradient from gigapascals within the wire to high vacuum outside is essential. Flow through an atomic-scale nozzle is dominated by friction, which raises the effective viscosity of the liquid metal to around that of tar, orders of magnitude higher than the metal's bulk value. Fortunately, that viscosity doesn't shut off the flow but reduces it to a slow, controlled trickle. The escaping drop, illustrated here in time-lapse images over several hundred seconds, grows from roughly 3 to 30 zeptoliters. Thanks to surface tension, the drop of molten metal hangs together, suspended by a thin meniscus thread.

The technological achievement—engineering a method to deliver a reproducibly small drop inside an instrument whose spatial resolution can distinguish atomic-scale processes—"is a tour de force that opens a new window on phase transformations," says Jim DeYoreo (Lawrence Livermore National Laboratory). Indeed, a drop of molten metal composed of between 10^4 and 10^6 atoms is small enough to exhibit significant deviations from the phase behavior of bulk alloys.

The expectation of interesting transformations is borne out in the Au–Ge system. Undercooling liquid metals is difficult, but the drop's free-hanging position isolates it from surfaces whose impurities and crevices might otherwise nucleate crystallization. While slowly cooled from its melting temperature of 350 °C down to just a few degrees above its 300 °C crystallization point, a drop roughly 30 nm in diameter can exhibit a striking phenomenon: the sudden emergence of planar facets that form and decay on the liquid's otherwise spherical surface. Further cooling then freezes the structure into a solid icosahedron whose shape closely matches the last positions of the transient facets.

One of Plato's perfect solids, the icosahedron is among the most efficient ways to pack atoms. With their fivefold symmetry, icosahedral clusters can't assemble into periodic crystals. And they are energetically metastable because of strain energy that accumulates with crystal size. But Uzi Landman (Georgia Institute of Technology) argues that theoretical considerations do not preclude the appearance of the facets on a liquid surface. In 1998 his group predicted the formation of a precursor icosahedral structure, at least for the reverse process of melting gold nanoclusters from the solid state. Moreover, as cluster sizes shrink, the surface-to-volume ratio grows and surface properties become increasingly likely to dominate the observed behavior, including how a liquid solidifies.

One of the hallmarks of a liquid metal, even at macroscopic scales, is the prevalence of ordered layers near the surface. Just last year, Oleg Shpyrko (Argonne National Laboratory) and colleagues measured sharp Bragg reflections from the first few monolayers of molten gold–silicon,[2] a cousin to Au–Ge alloy. The Sutters speculate that such short-range layering may lower the surface energy enough to cover the cost of the planar faceting in Au–Ge and prompt crystallization at its surface.

However, Friso van der Veen (Paul Scherrer Institute) emphasizes that the precise nucleation pathway remains unclear. With its lower surface tension, silicon preferentially segregates from gold, diffuses to the outermost surface, and accompanies the layering effect in the Au–Si system. With a similarly deep eutectic, Au–Ge alloy may be influenced by the same sort of segregation. A Ge-rich surface might naturally alter the crystallization temperature.

With various semiconductors and transition-metal catalysts available to them, the Sutters are now generalizing their pipette engineering to different elements and alloys for more insight.

Mark Wilson

References

1. P. W. Sutter, E. A. Sutter, *Nat. Mater.* **6**, 363 (2007).
2. O. G. Shpyrko et al., *Science* **313**, 77 (2006).